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- (54) **Improved Cladding Process and Product**
- (57) A clad substrate is produced by coating at least one of the facing surfaces of the cladding and substrate with boron, assembling the cladding on the substrate, resistance welding (e.g. capacitor discharge spot) the seams, subjecting the assembly to an elevated temperature for an extended time under vacuum so that the boron coated surface melts to form a liquid zone, and following the resulting gas-tight sealing at the seams diffusion bonding the assembly by HIP.

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SPECIFICATION
Advanced Cladding Process

The surface stability of superalloys is a significant problem for advanced industrial gas turbines. Highly corrosive environments are generated by the combustion of heavy fuel oils and when coupled with the higher firing temperatures and longer maintenance intervals, very strict limitations arise in material selection.

One solution to the surface stability problem involves the application of an oxidation and highly corrosion resistant sheet cladding alloy to a high strength substrate. Considerable progress has been made in the development of methods of diffusion bonding of cladding to such substrates. For example, Shilling et al. in U.S. Patent 3,928,901 teach a method in which the sheet cladding is cold isostatically pressed to form a tight skin over the substrate. Beltran et al. teach a process in which the cladding is applied, the space between the cladding and the substrate is evacuated, all seams are vacuum brazed, and thereafter the assembly is diffusion bonded in an autoclave using a gaseous medium and elevated temperature and pressure in U.S. Patent 3,904,101. Shilling et al. U.S. Patent 3,962,939, teach a process in which a preassembled sheet cladding and substrate is masked at all seams, surrounded with glass chips and then hot diffusion bonded to melt the glass and insure an isostatic stress state.

The cladding processes currently employed involve a relatively large number of steps, some of which are highly labor intensive and therefore costly. The techniques are also difficult to apply to the more complex configurations such as multi-vane nozzle segments. In some cladding processes low melting eutectic phases remain after cladding which are characteristically brittle at low temperatures. Inclusions of oxides and other materials at the cladding/substrate bond line may also be present.

It is the object of this invention to provide a new method for diffusion bonding sheet cladding to complex part configurations which eliminates several of the major steps employed in the prior art while simultaneously offering the capacity for cladding different substrate configurations easily and efficiently and to provide objects thus produced. This and other objects of the invention will become apparent to those skilled in the art from the following detailed description.

This invention relates to a method for diffusion bonding sheet claddings to substrates and to the cladded substrates thus produced. More particularly, the method involves the coating of at least one of the facing surfaces of the cladding and the substrate with boron, assembling the cladding to the object, and subjecting the resulting assembly to a time and temperature cycle sufficient to cause a liquid zone to form between the cladding and the substrate facing surfaces and a time-temperature-pressure hot

65 completely bond the cladding to the substrate. The process of the present invention is applicable to the manufacture of gas turbine buckets, multi-vaned nozzle segments where configurations are difficult to fabricate, certain 70 stages of ultrahigh temperature turbine hot gas path parts and the like. Such parts comprise a clad substrate of appropriate shape. The substrate is a metal casting and while the present invention is applicable to all types of metal castings, it is 75 particularly useful with castings prepared with the stronger alloys based on nickel, cobalt, or iron known in the industry as superalloys. Preparation of the casting itself is conventional and does not form part of this invention. Any casting or 80 cladding whose surface will accept a boron coating and which is also capable of accepting welding such as capacitor discharge welding can be used.

The preferred cladding materials are nickel-chromium alloys such as those commercially available from the International Nickel Company under the designations IN-671 and IN-617. These nickel-chromium alloys are essentially 50-80% by weight of nickel and 20-50% by 85 weight of chromium, with a preferred composition being 50% nickel and 50% chromium. The more complex alloys contain a number of elements and are typified by IN-617 which contains 22 wt.% chromium, 1 wt.% aluminum, 2.4 wt.% cobalt, 9 95 wt.% molybdenum, 0.003% boron, 0.07% carbon with the balance being nickel. Other cladding materials which can be used include Hastelloy-X, FeCrAlY (2541), HS 188,304 stainless steel, and the like. The cladding or substrate materials must 100 be capable of being coated with boron and also capable of accepting a weld such as from a capacitor discharge welding apparatus. By way of example, typical cladding thickness may range from approximately 0.005 to 0.050 inches and 105 preferably between 0.010 and 0.030 inches; however, other thickness may also be used without departing from the spirit of the present invention.

In the method of the present invention, 110 preferably one of the facing surfaces of the sheet cladding and the substrate, but possibly both, are coated with boron by any suitable conventional process. The boriding may be effected before or after the sheet cladding is shaped in the event 115 that the facing surface of the cladding is coated. Thereafter, the sheet cladding and substrate are assembled in conventional fashion, i.e., the cladding preform of appropriate composition and shape is prepared by suitable means such as 120 chemical etching, degreasing, abrading or nickel plating and the preform is placed over the substrate and the seams spot welded or resistance seam welded in such a manner as to provide as small a gap between the seams as is feasible. Generally, a gap of less than 1 mil can be achieved. The boron acts as a melting depressant for the surface of the material coated so that the object borided has a bulk melting temperature 125 shown that of the borided surface. When the

- assembly is subjected to a suitable combination of elevated temperature and extended time under vacuum, the surface melts to form a liquid zone followed by rapid isothermal solidification of the liquid phase because the boron has an extremely rapid diffusion rate due to its small atomic size (atomic radius 0.80 Angstrom) compared to other melting point depressants such as silicon or phosphorus. The result of the heat treatment and diffusion is a gas tight seal around the seams of the cladding. This gas tight seal allows a pressure differential to develop between the external and internal surfaces of the cladding during subsequent HIP. Thereafter, the diffusion bonded clad substrate is subjected to HIP, generally at preselected temperatures up to 2250°F and at preselected pressures up to about 30,000 psi for a time of application of, about 0.5—16 hours, such that there is no substantial degradation in the mechanical properties of the substrate after treatment but sufficient to cause the cladding to deform around the substrate and completely bond to it. Usually, the HIP cycle is effected at a temperature of about 1800—2250°F.
- 25 The present invention is characterized by precise control of the liquid phase, elimination of low melting eutectic phases which are characteristically brittle at low temperatures and by the break-up or dissolution of oxides and other inclusions at the cladding-substrate bond line.
- Control of the liquid phase is achieved by control of the quantity of boron which is coated on the cladding and/or substrate. Control of boron quantity controls the quantity of liquid phase present by the specific phase chemistries involved in the diffusion bonding coating. Sufficient boron is used to create enough liquid to form an effective gas tight seal between the cladding and the substrate but no more than necessary is used because greater quantities of boron could be deleterious to the substrate and cladding properties. In general, the boron is used in an amount sufficient to provide a nominal liquid phase of about 0.0002 to 0.004 inch in thickness and preferably between 0.0006 and 0.002 inch in thickness. The amount of boron necessary depends on the chemical composition of the particular materials bonded. For example, the amount of boron being selected should be sufficient to form a liquid seal between the seams of the claddings while minimizing the time/temperature required to diffuse away boron-rich phases.
- The elimination of low melting eutectic phases is accomplished by the use of boron as the only melting point depressant and by the time-temperature and pressure cycles which diffuse the boron into the cladding and substrate. As previously pointed out, the exclusive use of boron allows the isothermal solidification of the liquid phase to occur during the diffusion heat treatment and HIP cycle because the boron has an extremely rapid diffusion rate due to its small atomic size compared to other melting point depressants. In general, the diffusion heat treatment utilizes
- temperatures in the range of about 1900—2300°F, preferably about 2050°—2150°F for a time of about 0.05—20 hours, preferably about 0.1—4 hours.
- 70 Break-up of oxides and other inclusions at the interface of the cladding substrate is achieved by the presence of the boron containing liquid phase over the entire interfacial area of the cladding and substrate. In other cladding processes, a liquid phase is not present over this entire area. It is believed that the presence of the liquid phase at the interface breaks up the inclusions which may be present on the surface of either the cladding or the substrate by melting the metal immediately surrounding the inclusions. In addition, the liquid film inhibits surface oxidation due to liquid film coverage of the substrate in the elements of low oxide stability.
- In order to further illustrate the present invention, examples of the method and products of this invention are described below. It will be appreciated that throughout this specification and claims, all parts and percentages are given by weight and all temperatures are in degrees
- 85 Fahrenheit unless otherwise indicated.
- Example 1**
- A sheet of IN—671 cladding material (50% nickel, 50% chromium) 0.010±0.001 in. thick is cut to the rough size required for cold forming to a commercially available first stage turbine bucket air foil shape. The IN—671 preform is then cold formed in a series of progressive dies until it is within close conformance with the envelope (typically 0.01—0.02 inch) of the desired air foil shape. The shape cladding is then welded together to form an air foil shape which would slip over the commercial bucket.
- The welded IN—671 cladding is coated with 0.005 to 0.006 grams/inch² of diffused boron on
- 105 the inside surface only. After ultrasonic cleaning and degreasing of the coated cladding and bucket in freon, the cladding is assembled on the first stage bucket and capacitor discharge welded to the bucket with closely spaced welds.
- 110 The bucket and cladding is placed in a vacuum furnace which is evacuated to about 10⁻⁴ Torr and heated to 2075°F±25°F for ten minutes. The cycle produces a 0.0002 to 0.002 inch liquid zone at the boron coated cladding surface which seals the cladding to the bucket.
- After the furnace cools down, the bucket is removed and visually inspected for gaps around the cladding to bucket joints. The part is then
- 120 inspected by pressurizing to 300 psi in a helium pressure vessel and rapidly depressurizing and removing the bucket from the pressure vessel and submerging the bucket in methanol. The absence of bubbles indicates a leak tight seal between the cladding and bucket.
- 125 The bucket is then placed in a hot isostatic pressure vessel and heated to 2000°F under an argon pressure of 15 KSI and held under such conditions for 1—3 hours. The HIP cycle closes any porosity remaining between the cladding and

the bucket and completes diffusion of the boron away from the cladding to bucket interface thereby raising the melting temperature of the interface region. The bucket is then removed from the autoclave and ultrasonically inspected to detect any defects in the cladding to bucket bond.

Finally, the cladded bucket is aged at 24 hours at 1550°F to develop the mechanical properties of the superalloy substrate and the bucket lightly blended on a belt sanding machine to feather out the cladding weld and smooth out any wrinkles in the bonded cladding.

Example 2

A 0.03 ± 0.002 inch thick sheet of S—57 cladding material (25% Cr, 3% Al, 5% Ta, 10% Ni, 0.2% Y, balance Co) is cut to the rough size required for cold forming to a commercial first stage single vane nozzle. Three pieces are required, one for the air foil section, and one each for the two nozzle end walls. The three preforms are then cold formed on a series of progressive dies until they are within close conformance with the envelope of the desired air foil and end wall shapes. Sufficient material is left on each piece so that an overlap seam can be made between the air foil and the end wall cladding pieces.

The shaped cladding pieces are then coated with about 0.005—0.006 grams/inch² of diffused boron of the inner surface only. After ultrasonic cleaning and degreasing in freon of the coated cladding pieces and nozzle, the cladding pieces are assembled and capacitor discharge welded with closely spaced welds to the nozzle and to each other.

The nozzle and cladding are then placed in a vacuum furnace and heat treated at 10^{-4} Torr vacuum at $2100^{\circ}\text{F} \pm 25^{\circ}\text{F}$ for one hour. The cycle produces a $0.0002\text{--}0.002$ inch liquid zone at the boron coated cladding surface which seals the cladding pieces together and to the nozzle.

The nozzle is visually inspected for gaps around all of the cladding joints and also by the submersion in methanol process described in Example 1.

The nozzle is then subjected to HIP at 2050°F under an argon pressure of 15 KSI for 1—3 hours.

Various changes and modifications can be made in the method and process of this invention without departing from the spirit and scope thereof. The various embodiments which have

been described herein were for the purpose of further illustrating the invention but were not intended to limit it.

55 Claims

1. A method of applying a cladding to a substrate comprising coating at least one of the facing surfaces of the cladding and the substrate with boron, assembling the cladding to the substrate and subjecting the resulting assembly to a time and temperature cycle sufficient to cause a liquid zone to form between the cladding and the substrate facing surfaces.
2. A method as claimed in Claim 1 wherein the amount of boron coated is sufficient to create a nominal liquid zone of $0.0002\text{--}0.004$ inch thickness.
3. A method as claimed in Claim 1 or Claim 2 wherein said boron is the only melting point depressant for the surfaces of said cladding and said substrate present.
4. A method as claimed in any one of the preceding claims wherein the boron is coated such that the entire interfacial area of the cladding and substrate when assembled is coated.
5. A method as claimed in any one of the preceding claims, wherein said time of said time and temperature cycle is $0.05\text{--}20$ hours and said temperature of said time and temperature cycle is $1900\text{--}2300^{\circ}\text{F}$.
6. A method as claimed in Claim 5 wherein said time is $0.1\text{--}4$ hours and said temperature is $2050\text{--}2150^{\circ}\text{F}$.
7. A method as claimed in any one of the preceding claims, wherein said assembly, subsequent to said cycle, is subjected to hot isostatic pressing.
8. A method as claimed in any one of the preceding claims wherein said cladding and substrate are individually superalloys.
9. A method as claimed in any one of the preceding claims wherein said cladding is a nickel-chromium alloy.
10. A method of applying a cladding to a substrate as claimed in claim 1, substantially as hereinbefore described in any one of the Examples.
11. A cladding on a substrate when produced by a method as claimed in any one of the preceding claims.